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# CEMENT AND LIME

## MANUFACTURE

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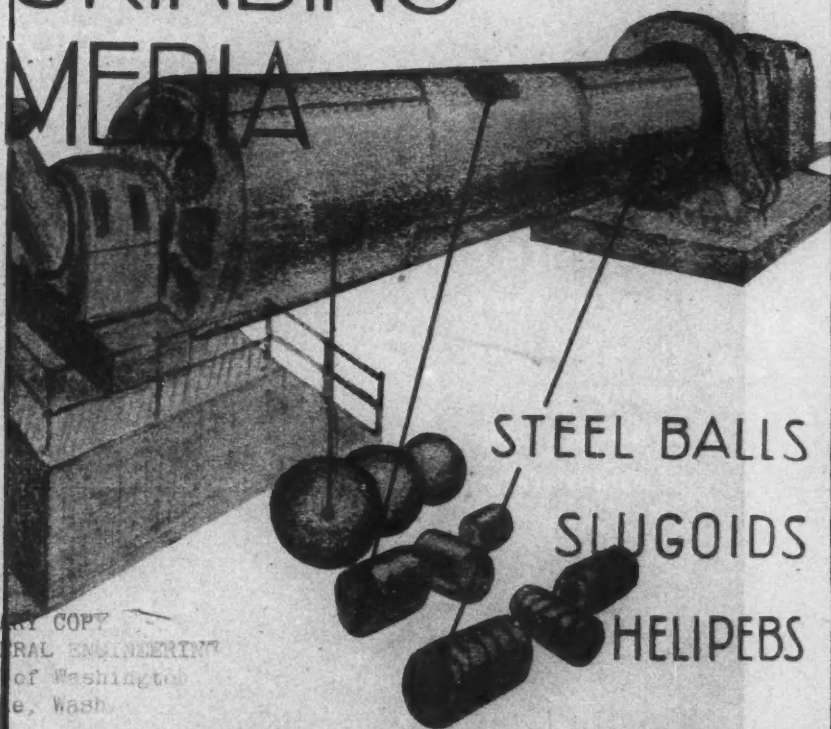
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# CEMENT AND LIME MANUFACTURE

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## The Wet-process Rotary Kiln.

THE shell of the rotary cement kiln does not yet appear to have any agreed form or shape. Kiln shells are made in many shapes. They vary in length from, say, 100 ft. to 500 ft., and some are even longer. They may be circular cylinders or have an enlargement for slurry at or near the feed end, or an enlargement for clinker at or near the exit end, or they may even have two such enlargements (one at each end) for the purposes named. Either form of shell will produce similar clinker at reasonable fuel consumption from slurry with the same moisture content if the kiln has skilled attention and the burning is intelligently carried out. It is even possible that the most unpromising shape of shell may, with good control, be more economical and operate at a lower fuel consumption than the most promising shape of shell with indifferent control.

In its fundamental form the kiln is fed with slurry made from finely-ground raw materials containing from 35 per cent. to, say, 43 per cent. of moisture; the kiln dries, heats, calcines, de-carbonates, and clinkers the slurry, and by suitable arrangements the kiln facilitates the cooling of the clinker. The range of temperature passed through during these processes is from, say, 60 deg. F. to 2400 deg. or 2450 deg. F. and then down to, say, 400 deg. F., depending upon the cooling facilities provided.

It is usual to heat the air for combustion by passing it through the clinker as the clinker is discharged from the kiln, and the weight and specific heat of these two elements are such that the temperature rise of the air is, with a reasonable tolerance owing to the factors involved, one-fourth or one-third of the temperature drop of the clinker.

The temperature of fusion, or clinkering, is of great importance, and although the amount of heat necessary for the process is small the intensity of the heat is of the utmost importance and the required temperature must be fully attained; the residual heat in the gases after the clinkering process has been completed has



proved amply sufficient for the succeeding processes of de-carbonating, calcining, drying, and heating that take place in the earlier part of the process.

With regard to the heat available within the kiln for other purposes after clinkering has been completed, an extended experiment was carried out on the Continent some years ago to determine if the whole of this heat could be usefully used, and for that purpose a compact kiln group was arranged comprising a long kiln (A), a short kiln (B), and a waste-heat boiler (C) as shown diagrammatically in *Fig. 1*. The material being processed was taken from kiln (A) by means of louvred openings arranged for quantity control and conveyed to kiln (B) into which it was deposited by scoop buckets, care being taken to reduce air leakage into the system as much as possible. The long kiln actually heated, dried, and partly calcined sufficient slurry for both kilns, and it also finished calcining and de-carbonated its share of the total product. The short kiln finished calcining, de-carbonated, and clinkered its share of the total product, and the waste gases were passed through the waste-heat boiler for the production of power. It would appear that the principal factor was the amount of fuel fed to

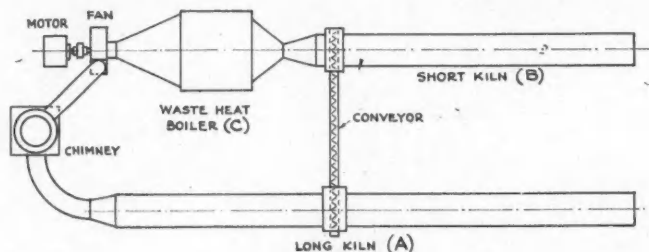


Fig. 1.

one or other of the kilns ; it is also possible that the amount of material being finally processed could be unequally divided, at will, between the two kilns. As no public report on the result is known to the writer, and as the system does not appear to have been continued, it may be assumed that it was not economical or there may have been no reason for its continuance after obtaining the information desired. It is known that the waste gases from the waste-heat boiler emerged at a lower temperature than those from a normal kiln not fitted with a chain system or its equivalent. Complete information on these tests would have considerable value.

*Fig. 2* is a section through a cylindrical kiln with typical temperature curves superimposed. These curves which are based upon those given by Dr. Hans Gygi in this journal for February, 1938, indicate the form and range of temperature likely to obtain for the material and the gases ; the firm line relates to the material and the dash line to the gases from the entry of the slurry until it passes out as clinker. The left-hand end of the dash line also shows the effect of a limited heat exchange system, for example, chains, upon the temperature of the gases ; in this case the temperature drop of the gases in passing through the system is 400 deg. to 500 deg. F. The value of this temperature drop lies in the more

advanced preparation, and possibly also the higher temperature, of the material being processed; the processes may even have advanced a part stage all through the system. The temperature drop of 400 deg. to 500 deg. F. is, of course, only typical, and it may be much greater if the heat exchange system is suitable and the raw material is acted upon without difficulty.

Changes in the rate of firing or in the quantity of slurry fed to the kiln are indicated by the temperature of the waste gases; that is if the quantity of fuel is increased the temperature will be higher, if the slurry is increased the temperature will be lower, and if both are increased proportionately the temperature may possibly remain constant. It is probable that many trials may be necessary with a new kiln before a satisfactory balance of the various factors is obtained and results in good day-to-day working conditions; balanced control and, more important still, continuous running are essential for efficient operation.

When the raw materials permit, the heat-exchange system should contribute

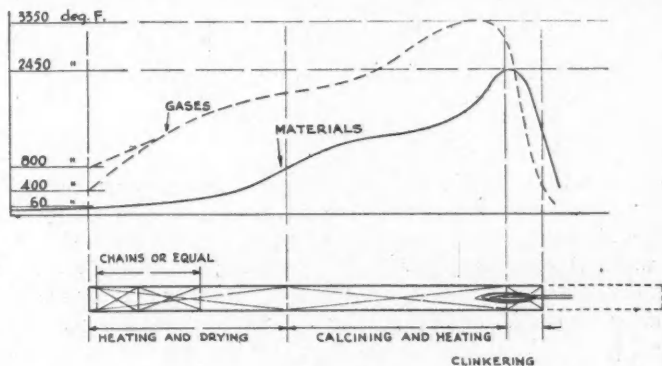


Fig. 2

to the breaking up of the dried slurry into small nodules of, say about  $\frac{1}{4}$  in. size, and so assist de-carbonating later.

Although Fig. 2 indicates the division of the kiln into zones, no such zones exist within the kiln or in the processes; in fact the process in any one zone may merge into that of the adjacent zone, both up-stream and down-stream, and the processes proceed simultaneously with much over-lapping. Also, any of the processes is somewhat arbitrary as knowledge of the time required for some parts of the processes is incomplete, but any time-lag or process-lag that may occur in one section may be made up in the succeeding sections; we do know, however, that high temperature, and in the later stages the highest temperature attainable, are distinctly advantageous.

Fig. 3 indicates a kiln having enlargements at the slurry end and at or near the clinkering end, a barrel of considerable length connecting these two enlargements. The varied form, dimensions, and position of these enlargements are invariably

the result of special consideration having been given to some aspect of the kiln's operation. The enlargement near the feed end is provided to facilitate the use of chains, lifters, desiccator, or other form of heat exchange for obtaining low exit-gas temperature without excessive throttling of the gas flow. These fittings must be designed to suit the characteristics of the raw materials that comprise the slurry; for example fittings suitable for use with limestone-shale slurry are most unsuitable or use with chalk-clay slurry, and vice versa, and marl slurry requires an entirely different equipment. Heat-exchange fittings generally need very careful selection as well as ingenuity in their application; a good purpose is therefore served if liberal space is provided for possible use later. The enlargement at the clinkering end is provided for holding and even cascading a large mass of material close to the high temperature flame so that continuous "heat-soaking" at the highest practicable temperature immediately previous to clinkering is assured.

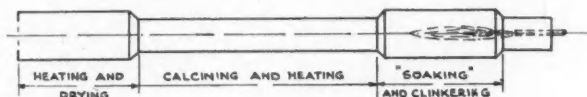


Fig. 3.

It is difficult to say which of these two enlargements is of the greatest value. There are several possible ways of obtaining the same result as is given by the slurry enlargement, but there is no other way of obtaining good and well-burnt clinker as both time and temperature have to be considered; it may be stated, however, that the earlier parts of the process may help the later part by breaking the drying slurry into small nodules so that the time necessary for the later part is reduced.

In many designs before the year 1939 the two enlargements had become almost standard practice, but enlargement at the slurry end is omitted in many later kilns, and although this change tends to simplification so far as construction, and possibly maintenance, are concerned, it is not certain that it will lead to more economical operation, and, although the barrel is being lengthened in some cases as a compensating feature or as a means of obtaining the same internal volume of the kiln, the increased length is unlikely to provide such good facilities for incorporating heat-exchange fittings later if they prove necessary, for these fittings usually require a larger diameter. In considering any diametral enlargement it may be pointed out that the position of any change of diameter may well prove to be a source of weakness especially in the area of high temperature.

Referring to the cylindrical kiln (Fig. 2), the following are typical basic figures in connection with the usual processes that take place in a normal kiln. They are "round" figures obtained by slide rule, but they serve the purpose of illustration; greater detail has little value from the practical point of view; and the omission of details prevents one from losing sight of principles.



## HEAT CONSUMPTION IN ROTARY KILN (WET PROCESS)

Weight of clinker produced .. .. .	2,240 lb.
Weight of raw material (dry) .. .. .	3,450 lb.
Ratio of these two quantities .. .. .	1 : 55
Slurry moisture .. .. .	40 per cent.
Weight of moisture .. .. .	(approx.) 2,260 lb.
Initial temperature .. .. .	60 deg. F.
Weight of gas expelled .. .. .	(approx.) 1,210 lb.
Waste-gas temperature .. .. .	400 deg. F.

The heat required for the separate processes, starting from the upper end of the kiln, is as follows :

(A) Raising the temperature of the moisture—	B.T.U.'s
Heating moisture from 60 deg. F. to 212 deg. F. .. .. .	343,295
Evaporating moisture at 212 deg. F. .. .. .	2,193,023
Superheating steam to 400 deg. F. .. .. .	200,922
Total .. .. .	2,737,240
(B) Raising the temperature of the raw material from 60 deg. F. to 1500 deg. F. B.T.U.'s	
Of the part that becomes gas .. .. .	347,089
Of the part that remains solid .. .. .	677,376
Decomposing $\text{CaCO}_3$ .. .. .	2,019,049
Total .. .. .	3,043,514
(C) Raising temperature of calcined material from 1500 deg. F. to 2400 deg. F. and clinkering .. .. .	443,520
Final total (say) .. .. .	6,224,000

On the basis of these figures we arrive at the following percentages of total heat used or required in the various sections : (A) 44, (B) 48.9, and (C) 7.1. It should be pointed out that these figures take no account of the exothermic heat produced or released in the materials at the higher temperature.

Note that the tables of heat consumption start at the slurry end where the temperature is the lowest and proceed towards the clinkering zone where the temperature is the highest. In practice combustion takes place in the clinkering zone, all the other processes take place in the order of descending temperature, and any heat in excess or unused is passed on for use in the succeeding stage. All the heat is used and the only apparent loss is the heat in the waste gases ; this, however, is hardly correct because if all the processes were more efficient the exit-gas temperature would be much higher enabling a larger heat exchange system to be used which in turn would result in greater temperature drop of the gases, and so the cause and effect would react upon each other and the processes would be generally improved. Apart from the clinkering zone and its approaches, in the earlier parts of the process heat at almost any temperature may be used.

Using the figures given and applying them to a kiln having a reputed coal consumption of 26 per cent. on the clinker produced, and using, say, 12 lb. of air per pound of coal, the weight of the exit-gases will be as much as  $5\frac{1}{2}$  tons per ton of clinker produced, the volume to a large extent depending upon the temperature of discharge. The weight of waste gases from a wet-process kiln producing 20 tons of clinker per hour will therefore be about 110 tons per hour.

## The Setting of Cement in the Presence of Large Quantities of Water.

In the "Bulletin d'Etudes et de Recherches Techniques" (No. 1, Bucharest, 1949) Dr. A. Steopoe considers the setting of cement in the presence of large quantities of water, and suggests a new method of overcoming the difference between the conditions under which cement is tested in a laboratory and is used in construction. Cement paste used in standard setting tests with the Vicat needle has 24 per cent. to 30 per cent. of water. In practical concrete mixtures the water-cement ratio may be from 0.4 to 1.0. A neat cement paste cannot be made with such a quantity of water because a solution is obtained in which the cement is a sediment. To determine the setting time of cement in these conditions, normal cement paste is placed in a porous pot which is placed in a vessel of water so that the paste can adsorb water without segregation and deposition of a sediment. The setting time is then determined by a Vicat needle. By this method the setting time is found to be longer than that determined by standard methods. The increase in initial setting time is about 10 per cent. and in final setting time about 45 per cent. The apparatus can also be used to study the effect of salt water on the setting of cement, but the presence of sodium chloride and calcium chloride, which according to the standard method causes a considerable reduction in the setting time, made little difference when the porous-pot method was used. Initial setting time is about the same, and the final setting time is reduced by only about 7 per cent.

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### Transport of Cement in Containers.

THE cement for two dams in Italy is being transported in cylindrical galvanised steel containers each containing 0.4 ton. The containers are filled automatically at the cement works and are loaded on to motor-driven trailers and taken to the railway by which they are conveyed on wagons to the station nearest to the site, where they are again loaded on to trailers. The containers are transferred from one vehicle to another on roller conveyors. At the site the cement is discharged from the containers into a small bin from which it is pumped to a 2,000-tons silo at the concrete plant. According to a report in "Travaux," about 200 tons of cement are delivered daily, 12 wagons and 920 containers being used.

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### Dust Recovery.

A NEW brochure on dust and fume control and recovery has been issued by The Power Gas Corporation, Ltd., of Stockton-on-Tees. Illustrations are given of the company's equipment installed in different industries, and diagrams show arrangements of dust removal installations. Some tables and data of use in connection with the design of dust-control plant are included.

## Proportioning of Raw Mixtures for Portland Cement.

THE accompanying tables and the methods of calculation described in the following have been found useful for determining the proportions of raw materials of known composition for the manufacture of Portland cement.

The more important points to be observed when selecting raw materials are :

(1) Limestone or other calcareous deposits high in magnesium carbonate content are generally unsuitable, as an MgO content in Portland cement of more than 5 per cent. is considered deleterious and is limited to between 3 per cent. and 5 per cent. in most specifications.

(2) Deposits containing zinc or lead or their compounds should be avoided.

(3) Phosphates, sulphates, sulphides, and alkalis should be present only in small amounts.

(4) Overburden consisting of loam, coarse sand, and pebbles should be removed from calcareous deposits before quarrying.

(5) Clay or marl containing appreciable amounts of coarse sand should either be rejected or be finely ground.

Where two materials only are to be considered, their evaluation consists of accurate analysis and a few simple calculations to determine the limits of clinker composition available. With the modern trend towards special cements, the specifications for which set limitations upon the chemical composition, a third raw material has become common, a fourth is in use in some cases, and it is possible that others may have to be considered.

The major constituents of clinker are believed at present to be combined in the form of tricalcium silicate ( $3\text{CaO} \cdot \text{SiO}_2 = \text{C}_3\text{S}$ ), dicalcium silicate ( $2\text{CaO} \cdot \text{SiO}_2 = \text{C}_2\text{S}$ ), tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 = \text{C}_3\text{A}$ ), and tetracalcium aluminoferrite ( $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 = \text{C}_4\text{AF}$ ). The composition of these compounds is frequently required and the percentages of each of the oxides are given in *Table No. 1*.

The compound composition, calculated from the oxide composition of the clinker or cement, on the assumption of complete combination, is referred to as the potential composition. The equations for calculating potential composition for raw materials, clinkers, and cements used are :

$$\text{C}_3\text{S} = 4.0710\text{CaO} - 7.6024\text{SiO}_2 - 1.4297\text{Fe}_2\text{O}_3 - 6.7186\text{Al}_2\text{O}_3 \quad \text{Table No. 2}$$

$$\text{C}_2\text{S} = 2.8675\text{SiO}_2 - 0.75435\text{C}_3\text{S} \quad \dots \dots \dots \text{Table No. 3}$$

$$\text{C}_3\text{A} = 2.6504\text{Al}_2\text{O}_3 - 1.6920\text{Fe}_2\text{O}_3 \quad \dots \dots \dots \text{Table No. 4}$$

$$\text{C}_4\text{AF} = 3.0432\text{Fe}_2\text{O}_3 \quad \dots \dots \dots \text{Table No. 5}$$

*Tables Nos. 2 to 5* give the numerical values of the products for known percentages of the constituents, and use of the tables reduces considerably the work of computing the potential compositions.

In considering raw mixture compositions for Portland cement clinker, the following factors should be borne in mind.

(1) LIME SATURATION AND TOTAL SILICATES.—The potential amounts of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  represent the degree of lime saturation. High potential  $\text{C}_3\text{S}$  is

TABLE 1.—COMPOSITION OF OXIDES (PER CENT.)

Compound	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
CaO	73.7	65.1	62.3	46.15
SiO <sub>2</sub>	26.3	34.9	—	—
Al <sub>2</sub> O <sub>3</sub>	—	—	37.7	21.00
Fe <sub>2</sub> O <sub>3</sub>	—	—	—	32.85

TABLE 2.—FACTORS FOR TRICALCIUM SILICATE (C<sub>3</sub>S).

				CaO × 4.0710						
	α	1	2	3	4	5	6	7	8	9
10	40.71	44.78	48.85	52.92	56.99	61.07	65.14	69.21	73.28	77.35
20	81.42	85.49	89.56	93.63	97.70	101.78	105.85	109.92	113.99	118.06
30	122.13	126.20	130.27	134.34	138.41	142.49	146.57	150.63	154.70	158.77
40	162.84	166.91	170.98	175.05	179.12	183.20	187.27	191.34	195.41	199.48
50	203.55	207.62	211.69	215.76	219.83	223.91	227.98	232.05	236.12	240.19
60	244.26	248.33	252.40	256.47	260.54	264.62	268.69	272.76	276.83	280.90
70	284.97	289.04	293.11	297.18	301.25	305.33	309.40	313.47	317.54	321.61
80	325.68	329.75	333.82	337.89	341.96	346.04	350.11	354.18	358.25	362.32
90	366.39	370.46	374.53	378.60	382.67	386.74	390.82	394.89	398.96	403.03
					SiO <sub>2</sub> × 7.6024					
10	76.02	83.63	91.23	98.83	106.43	114.04	121.64	129.24	136.84	144.45
20	152.05	159.65	167.25	174.86	182.46	190.06	197.66	205.26	212.87	220.45
30	228.07	235.67	243.28	250.88	258.48	266.08	273.69	281.29	288.89	296.49
40	304.10	311.70	319.30	326.90	334.51	342.11	349.71	357.31	364.92	372.52
50	380.12	387.72	395.32	402.93	410.53	418.13	425.73	433.34	440.94	448.54
60	456.14	463.75	471.35	478.95	486.55	494.16	501.76	509.36	516.96	524.57
70	532.17	539.77	547.37	554.98	562.58	570.18	577.78	585.38	592.99	600.59
80	608.19	615.79	623.40	631.00	638.60	646.20	653.81	661.41	669.01	676.61
90	684.22	691.82	699.42	707.02	714.63	722.22	729.83	737.43	745.04	752.64
					Fe <sub>2</sub> O <sub>3</sub> × 1.4297					
10	14.30	15.73	17.16	18.59	20.02	21.45	22.88	24.30	25.73	27.16
20	28.59	30.02	31.45	32.88	34.31	35.74	37.17	38.60	40.03	41.46
30	42.89	44.32	45.75	47.18	48.61	50.04	51.47	52.90	54.33	55.76
40	57.19	58.62	60.05	61.48	62.91	64.34	65.77	67.20	68.63	70.06
50	71.49	72.91	74.34	75.77	77.20	78.63	80.06	81.49	82.92	84.35
60	85.79	87.21	88.64	90.07	91.50	92.93	94.36	95.79	97.22	98.65
70	100.08	101.51	102.94	104.37	105.80	107.23	108.66	110.09	111.52	112.95
80	114.38	115.81	117.24	118.67	120.09	121.52	122.95	124.38	125.81	127.25
90	128.67	130.10	131.53	132.96	134.39	135.82	137.25	138.68	140.11	141.54
					Al <sub>2</sub> O <sub>3</sub> × 6.7186					
10	67.19	73.90	80.62	87.34	94.06	100.78	107.50	114.22	120.93	127.65
20	134.37	141.09	147.81	154.53	161.25	167.97	174.68	181.40	188.12	194.84
30	201.56	208.28	215.00	221.71	228.43	235.15	241.87	248.59	255.31	262.03
40	268.74	275.46	282.18	288.90	295.62	302.34	309.06	315.77	322.49	329.21
50	335.93	342.65	349.37	356.09	362.80	369.52	376.24	382.96	389.68	396.40
60	403.12	409.83	416.55	423.27	429.99	436.71	443.43	450.15	456.86	463.58
70	470.30	477.02	483.74	490.46	497.18	503.90	510.61	517.33	524.05	530.77
80	537.49	544.21	550.93	557.64	564.36	571.08	577.80	584.52	591.24	597.96
90	604.67	611.39	618.11	624.83	631.55	638.27	644.99	651.70	658.42	665.14

TABLE 3.—FACTORS FOR DICALCIUM SILICATE ( $C_2S$ ).

					$SiO_2 \times 2.8675$					
	0	1	2	3	4	5	6	7	8	9
10	28.68	31.54	34.41	37.28	40.15	43.01	45.88	48.75	51.62	54.48
20	57.35	60.22	63.09	65.95	68.82	71.69	74.56	77.42	80.29	83.16
30	86.03	88.89	91.76	94.63	97.50	100.36	103.23	106.10	108.97	111.83
40	114.70	117.57	120.44	123.30	126.17	129.04	131.91	134.77	137.64	140.51
50	143.38	146.24	149.11	151.98	154.85	157.71	160.58	163.45	166.32	169.18
60	172.05	174.92	177.79	180.65	183.52	186.39	189.26	192.12	194.99	197.86
70	200.73	203.59	206.46	209.33	212.20	215.06	217.93	220.80	223.67	226.53
80	229.40	232.27	235.14	238.00	240.87	243.74	246.61	249.47	252.34	255.21
90	258.08	260.94	263.81	266.68	269.55	272.41	275.28	278.15	281.02	283.88
					$C_2S \times 0.75435$					
10	7.54	8.30	9.05	9.81	10.56	11.32	12.07	12.82	13.58	14.33
20	15.09	15.84	16.60	17.35	18.10	18.86	19.61	20.37	21.12	21.88
30	22.63	23.38	24.14	24.89	25.65	26.40	27.16	27.91	28.67	29.42
40	30.17	30.93	31.68	32.44	33.19	33.95	34.70	35.45	36.21	36.96
50	37.72	38.47	39.23	39.98	40.73	41.49	42.27	43.00	43.75	44.51
60	45.26	46.02	46.77	47.52	48.28	49.03	49.79	50.54	51.30	52.05
70	52.80	53.56	54.31	55.07	55.82	56.58	57.33	58.08	58.84	59.59
80	60.35	61.10	61.86	62.61	63.37	64.12	64.87	65.63	66.38	67.14
90	67.89	68.65	69.40	70.15	70.91	71.66	72.42	73.17	73.93	74.68

TABLE 4.—FACTORS FOR TRICALCIUM ALUMINATE ( $C_3A$ ).

					$Al_2O_3 \times 2.6504$					
	0	1	2	3	4	5	6	7	8	9
10	26.50	29.15	31.80	34.46	37.11	39.76	42.41	45.06	47.71	50.36
20	53.01	55.66	58.31	60.96	63.61	66.26	68.91	71.56	74.21	76.86
30	79.51	82.16	84.81	87.46	90.11	92.76	95.41	98.06	100.72	103.37
40	106.02	108.67	111.32	113.97	116.62	119.27	121.92	124.57	127.22	129.87
50	132.52	135.17	137.82	140.47	143.12	145.77	148.42	151.07	153.72	156.37
60	159.02	161.67	164.32	166.98	169.63	172.28	174.93	177.58	180.23	182.88
70	185.53	188.18	190.83	193.48	196.13	198.78	201.43	204.08	206.73	209.38
80	212.03	214.68	217.33	219.98	222.63	225.28	227.93	230.58	233.24	235.89
90	238.54	241.19	243.84	246.49	249.14	251.79	254.44	257.09	259.74	262.39
					$Fe_2O_3 \times 1.6920$					
10	16.92	18.61	20.30	22.00	23.69	25.38	27.07	28.76	30.46	32.15
20	33.84	35.53	37.22	38.92	40.61	42.30	43.99	45.68	47.38	49.07
30	50.76	52.45	54.14	55.84	57.53	59.22	60.91	62.60	64.30	65.99
40	67.68	69.37	71.06	72.76	74.45	76.14	77.83	79.52	81.22	82.91
50	84.60	86.29	87.98	89.68	91.37	93.06	94.75	96.44	98.14	99.83
60	101.52	103.21	104.90	106.60	108.29	109.98	111.67	113.36	115.06	116.75
70	118.44	120.13	121.82	123.52	125.21	126.90	128.59	130.28	131.98	133.67
80	135.36	137.05	138.74	140.44	142.13	143.82	145.51	147.20	148.90	150.59
90	152.28	153.97	155.66	157.36	159.05	160.74	162.43	164.12	165.82	167.51



TABLE 5.—FACTORS FOR TETRACALCIUM ALUMINO-FERRITE ( $C_4AF$ ).

				$Fe_2O_3 \times 3.0432$						
	0	1	2	3	4	5	6	7	8	9
10	30.43	33.48	36.52	39.56	42.60	45.65	48.69	51.73	54.78	57.82
20	60.86	63.91	66.95	69.99	73.04	76.08	79.12	82.17	85.21	88.25
30	91.30	94.34	97.38	100.43	103.47	106.51	109.56	112.60	115.64	118.68
40	121.73	124.77	127.81	130.86	133.90	136.94	139.99	143.03	146.07	149.12
50	152.16	155.20	158.25	161.29	164.33	167.38	170.42	173.46	176.51	179.55
60	182.59	185.64	188.68	191.72	194.76	197.80	200.85	203.89	206.94	209.98
70	213.02	216.07	219.11	222.15	225.20	228.24	231.28	234.33	237.37	240.41
80	243.46	246.50	249.54	252.59	255.63	258.67	261.72	264.76	267.80	270.84
90	273.89	276.93	279.97	283.02	286.06	289.10	292.15	295.19	298.23	301.28

considered necessary for high early strength and nearly all the hardening properties are attributed to silicates.

(2) THE ALUMINA, OR POTENTIAL  $C_3A$  CONTENT.—The potential  $C_3A$  content affects the setting and hardening properties. For low heat and sulphate-resistant cements it is desirable to keep the  $C_3A$  content as low as possible.

(3) THE FLUX AVAILABLE.—The flux is the liquid present at clinkering temperatures. The following formula for liquid at 1450 deg. C. is given by Lea and Desch:

$$\text{Liquid} = 1.13C_3A + 1.35 C_4AF + MgO + \text{alkalis.}$$

The importance of the potential liquid and its relation to the ease of burning is well recognised, and any normal composition with 25 per cent. or more liquid should not be difficult to clinker.

(4)  $MgO$  CONTENT.—Although  $MgO$  acts as a flux, it is also a potential source of delayed expansion. For this reason nearly all specifications set a maximum limit to the  $MgO$  content, usually between 3 per cent. and 5 per cent.

(5) OTHER SPECIFICATION LIMITS.—Specifications for special types of cement set limits on the  $C_3A$  content and on the ratio  $\frac{Al_2O_3}{Fe_2O_3}$ .

(6) COAL ASH AND DUST.—When pulverized fuel is used in the burning process, part of the coal ash is deposited with the raw mixture and is brought forward to the burning zone where it becomes part of the clinker produced. In addition, some of the raw material is picked up by the kiln gases and is carried out of the kiln. This changes the composition, since the fine particles so removed are not of the same composition as the raw mixture as a whole. As a result of the combined effect of coal ash and dust loss, or dust alone where gas or oil is used, the potential composition of the clinker will differ from that of the raw mixture fed to the kiln. To determine what this difference would be, the potential compositions of the kiln feed and clinker produced should be compared over a period of steady operation. Adjustments can then be made to the mixture to give the required potential clinker composition.

It will be evident that in order to control  $n$  potential compounds it is necessary to proportion  $n + 1$  suitable raw materials. Where the chemical composition of

the raw materials is entirely suitable, the algebraic method of calculating the proportions, requiring the solution of simultaneous equations, may be used. If, however, this method produces a negative value for one of the raw materials in the solution, the desired composition cannot be obtained with those raw materials and a change in one or other of them is necessary. The method of calculation illustrated in the following indicates, as the calculations proceed, how closely to the desired composition the available raw materials can be proportioned.

### Example.

As an example of the method of calculation, it will be assumed that the raw materials available are chalk, clay, pyrites cinders, and loam having the chemical analysis, calculated as dry and ignited, given in *Table No. 6*. The potential composition of the clinker required to be produced from these materials is  $C_3S$ , 55 per cent. ;  $C_3A$ , 4 per cent. ;  $C_4AF$ , 12 per cent. The clinker is to be produced in a kiln using pulverized fuel. It has been found from previous tests that the clinker produced contains 2.7 per cent. of coal ash. The partial analysis and potential compound composition of this coal ash are as follows:  $SiO_2$ , 40 per cent. ;  $Al_2O_3$ , 25 per cent. ;  $Fe_2O_3$ , 15 per cent. ;  $CaO$ , 12 per cent. ;  $MgO$ , 2 per cent. ;  $C_3S$ , — 444.7 per cent. ;  $C_2S$ , 450.1 per cent. ;  $C_3A$ , 40.9 per cent. ;  $C_4AF$ , 45.7 per cent. Allowing for 2.7 per cent. of this ash being taken up in the clinker, the potential loss-free slurry compound composition required is  $C_3S$ , 68.9 per cent. ;  $C_3A$ , 3.0 per cent. ;  $C_4AF$ , 11.1 per cent.

The next stage is to calculate the potential compound composition of the ignited raw materials, using *Tables Nos. 2 to 5*. The computed compositions are given in *Table No. 7*, from which it is seen that the materials, with the exception of the chalk, are deficient in lime, so that the next stage is to combine the chalk with each of the argillaceous materials separately to bring the potential  $C_3S$  content to the required amount of 68.9 per cent. in each of the three primary mixtures. The proportions are found by using the formula

$$x = \frac{A - R}{A - B}$$

where  $x$  is the proportion of No. 2 material,  $A$  is the percentage of desired compound in No. 1 material,  $B$  the percentage of desired compound in No. 2 material, and  $R$  is the percentage of desired compound required in the mixture. The calculations of the chalk plus clay mixture to give 68.9 per cent.  $C_3S$  are given in *Table No. 8*, and the results are transferred to column (2), *Table No. 9*.

The other two primary mixtures, chalk plus pyrites cinders and chalk plus loam, are calculated in a similar manner, and the proportions and potential compound compositions of these mixtures are given in columns (3) and (4) in *Table No. 9*.

From an examination of the potential compound compositions of these three mixtures it is apparent that in order to obtain a  $C_3A$ -content of 3 per cent. there are two possibilities, namely (1) to combine the chalk plus clay mixture with the chalk plus cinders mixture, and (2) to combine the chalk plus cinders mixture with the chalk plus loam mixture. Since the  $C_3A$  contents of the chalk plus clay

TABLE 6.—EXAMPLE OF CHEMICAL ANALYSIS OF RAW MATERIALS.

	Chalk		Clay		Pyrites cinders		Loam	
	Dry	Ignited	Dry	Ignited	Dry	Ignited	Dry	Ignited
SiO <sub>2</sub>	1.2	2.11	57.2	65.83	15.3	15.48	81.0	83.26
Al <sub>2</sub> O <sub>3</sub>	0.4	0.70	14.8	17.03	1.1	1.12	11.4	11.71
Fe <sub>2</sub> O <sub>3</sub>	0.3	0.53	5.9	6.79	81.0	81.98	1.9	1.95
CaO	54.0	94.73	4.7	5.41	0.0	0.00	0.5	0.51
MgO	0.5	0.88	1.6	1.84	0.0	0.00	0.2	0.21
Ignition loss	43.0	—	13.1	—	1.2	—	2.7	—
Undetermined	0.6	1.05	2.7	3.10	1.4	1.42	2.3	2.36
Total	100.0	100.00	100.0	100.00	100.0	100.00	100.0	100.00

TABLE 7.—EXAMPLE: POTENTIAL COMPOUND COMPOSITION OF RAW MATERIALS.

Material	C <sub>2</sub> S	C <sub>3</sub> S	C <sub>2</sub> A	C <sub>4</sub> AF	MgO	Balance	Total
Chalk .. ..	364.1	-268.6	1.0	1.6	0.9	1.0	100.0
Clay .. ..	-602.6	643.3	33.7	20.7	1.8	3.1	100.0
Pyrites cinders	-242.4	227.2	-135.7	249.5	Nil	1.4	100.0
Loam .. ..	-712.3	776.1	27.7	5.9	0.2	2.4	100.0

TABLE 8.—EXAMPLE OF CHALK + CLAY MIXTURE.

Material	C <sub>2</sub> S		Proportion	C <sub>2</sub> S	C <sub>3</sub> S	C <sub>2</sub> A	C <sub>4</sub> AF	MgO	Undetermined	Total
Chalk	(A) 364.1	(A-R) 295.2	0.6946	252.9	-186.56	0.69	1.11	0.63	0.69	69.46
Clay	(B) -602.6	(A-B) 966.7	$\frac{(A-R)}{(A-B)}$ 0.3054	-184.0	196.40	10.31	6.32	0.55	0.96	30.54
Required	(R) 68.9		1.0000	68.9	9.84	11.00	7.43	1.18	1.65	100.00

TABLE 9.—EXAMPLES OF VARIOUS MIXTURES.

(1) Mixture	(2) Chalk Clay	(3) Chalk Cinders	(4) Chalk Loam	(5) Chalk + Clay Chalk + Cinders	(6) Chalk + Loam Chalk + Cinders
Proportions (per cent.)	69.46 Chalk 30.54 Clay	51.34 Chalk 48.66 Cinders	72.58 Chalk 27.42 Loam	89.55 (Chalk + Clay) 10.45 (Chalk + Cinders)	92.79 (Chalk + Loam) 7.21 (Chalk + Cinders)
C <sub>2</sub> S	68.90	68.90	68.90	68.90	68.90
C <sub>3</sub> S	9.84	-27.24	17.91	5.95	14.65
C <sub>2</sub> A	11.00	-65.53	8.33	3.00	3.00
C <sub>4</sub> AF	7.43	122.22	2.78	19.44	11.40
MgO	1.18	0.46	0.70	1.11	0.68
Undetermined	1.65	1.19	1.38	1.60	1.37
Total	100.00	100.00	100.00	100.00	100.00

mixture and the chalk plus loam mixture are both over 3 per cent., direct proportioning of these will not produce the required composition. Proceeding in the same way as shown for the chalk plus clay mixture, the proportions and potential compound compositions of the secondary mixtures are found to be as in columns (5) and (6) of Table No. 9.

It is seen that it is not possible to produce a mixture having the required  $C_4AF$ -content of 11.1 per cent. in the ignited slurry. Had the algebraic method of proportioning been used there would have been a negative result for one of the raw materials. The method illustrated indicates that the materials can be proportioned to give the required  $C_3S$  and  $C_3A$  contents and  $C_4AF$  between the limits of 11.4 per cent. and 19.44 per cent. Practical considerations would probably prevent the use of a chalk plus cinder plus loam mixture alone, and the highest proportion of this secondary mixture would probably be 50 per cent. Assuming, therefore, that the two secondary mixtures are proportioned in equal parts, the final composition will be as follows:

Mixture	Proportions per cent.	$C_3S$	$C_2S$	$C_3A$	$C_4AF$	MgO	Undetermined	Total
(Chalk + clay) + (chalk + cinders) .. ..	50	68.9	10.3	3.0	15.4	0.9	1.5	100.0
(Chalk + loam) + (Chalk + cinders) .. ..	50							

The final proportions of the various materials, calculated on the ignited and dry basis, will then be as follows:

$$\text{Chalk.}-(1) 0.6946 \times 0.8955 \times 0.50 = 0.31103$$

$$(2) 0.5134 \times 0.1045 \times 0.50 = 0.02682$$

$$(3) 0.5134 \times 0.07214 \times 0.50 = 0.01851$$

$$(4) 0.7258 \times 0.9279 \times 0.50 = 0.33662$$

$$\hline 0.69298 = 1.2150 \text{ dry chalk.}$$

$$\text{Clay.}-0.3054 \times 0.8955 \times 0.50 = 0.13678 = 0.1574 \text{ dry clay.}$$

$$\text{Cinders.}-(1) 0.4866 \times 0.1045 \times 0.50 = 0.02541$$

$$(2) 0.4866 \times 0.07214 \times 0.50 = 0.01755$$

$$\hline 0.04296 = 0.0435 \text{ dry cinders.}$$

$$\text{Loam.}-0.2742 \times 0.92786 \times 0.50 = 0.12728 = 0.1308 \text{ dry loam.}$$

$$\hline 1.5467$$

Thus the proportions of dry raw material are: chalk, 78.56 per cent.; clay, 10.18 per cent.; pyrites cinders, 2.81 per cent.; loam, 8.45 per cent.; and the analysis of the dry slurry (in percentages) is:  $SiO_2$ , 14.04;  $Al_2O_3$ , 2.82;  $Fe_2O_3$ , 3.28;  $CaO$ , 42.94;  $MgO$ , 0.57; ignition loss, 35.37; undetermined, 0.98; (total, 100).

The clinker analysis and potential compound composition (in percentages).

after allowing for 2.7 per cent. of coal-ash being taken up by the raw material in its passage through the kiln, are :

Analysis— $\text{SiO}_2$ , 22.21 ;  $\text{Al}_2\text{O}_3$ , 4.92 ;  $\text{Fe}_2\text{O}_3$ , 5.34 ;  $\text{CaO}$ , 64.98 ;  $\text{MgO}$ , 0.91 ; undetermined, 1.64 ; (total, 100).

Potential composition— $\text{C}_3\text{S}$ , 55.0 ;  $\text{C}_2\text{S}$ , 22.2 ;  $\text{C}_3\text{A}$ , 4.0 ;  $\text{C}_4\text{AF}$ , 16.25. British Standard lime saturation = 90.78 per cent. Silica ratio =  $\frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3} = 0.92$  per cent.

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### The Hydration of Tricalcium Aluminate.

In the setting of Portland cement, the role of tricalcium aluminate, although only a secondary constituent, has long been recognised, but there is a lack of agreement between the results of investigations of its hydration. Experiments made at the laboratories of the Building and Public Works authorities of Paris and reported by the chief chemist, M. J. Brocard, in a recent number of "Verres et Silicates" had the object of studying the hydration of tricalcium aluminate at temperatures from 15 deg. C. to 100 deg. C. To cause carbonation, the greatest possible contact with the air was effected. A mechanically-agitated thermostat and distilled water free from carbonic anhydride were used. The product was prepared by heating to 1500 deg. C. a mixture of calcium carbonate and pure alumina, giving a molecular ratio  $\text{CaO} : \text{Al}_2\text{O}_3$  equal to three. The product was crushed until it all passed a sieve having 4,900 meshes per square centimetre. Although the temperature did not exceed 1500 deg. C., radio-crystallographic analysis revealed the presence of traces of pentacalcium-trialuminate ( $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ ).

The conclusions drawn from the results of the tests are that tricalcium aluminate in the presence of water at ordinary temperatures gives, after a few minutes, a supersaturated solution that permits the deposition of small hexagonal crystals of tricalcium-aluminate,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ . In lime-water tetracalcium-aluminate ( $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ ) is obtained. At higher temperatures up to 100 deg. C. the reaction is accelerated and becomes almost instantaneous as the upper limiting temperature is approached.

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## **Air-entraining Cement and Air-entrained Concrete.**

THE inclusion of a limited amount of air in Portland cement concrete is being increasingly practised in America and results in an improvement in some of the properties of concrete and a diminution in others. Workability, resistance to frost and to some chemicals, and homogeneity are improved, but impermeability and strength, for the same water-cement ratio, are reduced. The increase in workability makes possible a reduction in the amount of water and fine aggregate and therefore loss of strength may be prevented. Thermal properties and resistance to abrasion are apparently unaltered. The air may be entrained by using a Portland cement in which an agent has been added during manufacture, or by adding the agent to the concrete at the time of mixing. Since variations in the grading of the aggregate, the proportions of the mixture, the method and duration of the mixing, the consistency, and other factors affect the amount of air entrained, many engineers in the United States appear to prefer the second method.

Air entrainment results in small disconnected bubbles of air being formed in the concrete and is said to be most satisfactory when the action of the agent does not depend on chemical reaction with the cement. The agents used most commonly in America appear to be Vinsol resin, a neutralised natural wood resin, and Darex, particulars of the composition of which are not available, and both are permitted by official standards to be used with Portland cement. Other materials are animal and vegetable fats and oils and their fatty acids, various wetting agents, and water-soluble soaps of resin acids.

### **American Standards for Air-entraining Portland Cement.**

The standards of the United States for air-entraining Portland cements are those of the American Society for the Testing of Materials and those of the Federal authorities. The A.S.T.M. Standards C175-47T (tentative) for air-entraining Portland cements are Type IA for use in concrete exposed to the action of severe frosts and Type IIA for use in concrete required to have a moderate resistance to sulphate attack or a moderate heat of hydration. The Federal Specification No. SS-C-192 includes air-entraining Portland cements of the following types: Type IA for general use; Type IIA for use in concrete required to have a moderate resistance to sulphate attack or a moderate heat of hydration; Type IIIA, rapid-hardening Portland cement; Type IVA, Portland cement having a low heat of hydration; and Type VA, high sulphate-resistant Portland cement.

**CHEMICAL COMPOSITION.**—The chemical composition, including the maximum amount of insoluble residue and loss on ignition, is the same as that for the corresponding types of Portland cements without air-entraining agents as given in this journal for May, 1949 (A.S.T.M. standards) and July, 1949 (Federal specifications). The A.S.T.M. standards permit not more than 0.05 per cent. of Darex air-entraining agent; the content of Vinsol resin permitted is such as to give an air-content of the mortar between 15 per cent. and 21 per cent. by volume, the exact amount depending on the air-content required. The Federal specifications permit less than 1 per cent. of air-entraining agent, which may be any agent approved by the

purchaser. The maximum air-entrainment for cements without an agent is 8 per cent. by volume, and from 12 per cent. to 20 per cent. if an agent is used. Air-entraining Portland cements complying with these standards are said to entrain a suitable amount of air in concrete containing from 420 lb. to 610 lb. of cement per cubic yard.

PHYSICAL PROPERTIES.—The fineness, setting times, and soundness are the same as for the corresponding types of cements without air-entraining agents as given in this journal for May and July, 1949. Tensile-strength tests are not specified in either standard and, except for low-heat and sulphate-resistant cements (Types IVA and VA), lower compressive strengths, as given in Table I, are accepted.

TABLE I.—MINIMUM COMPRESSIVE STRENGTHS OF AIR-ENTRAINING PORTLAND CEMENTS.

Standard		Type of cement	Compressive strengths (lb. per square inch). Age of specimen in days				Compressive strengths (kg. per square centimetre). Age of specimen in days			
A.S.T.M. (1947)	Federal (1946)		1	3	7	28	1	3	7	28
IA	IA	O	—	750	1500	3000*	—	53	105	211*
IIA	IIA	Mod. sulphate resistant and mod. low heat	—	600	1250	2500*	—	42	88	176*
—	IIIA	Rapid-hardening	1100	2200	—	—	77	155	—	—
—	IVA	Low heat	—	—	800	2000	—	—	56	141
—	VA	Sulphate resistant	—	—	1000	2200	—	—	70	155

\* 28-day test made only on request.

A summary of experience in the United States regarding air-entraining cements and agents is given by Mr. J. F. Barbee in the "Journal of the American Concrete Institute" for April, 1949, and includes the following conclusions.

The quantity of air entrained depends upon the type and grading of the aggregate, the cement content, the type of cement, the consistency of the mixture, the method and time of mixing, and the type and amount of air-entraining agent used. The amount of entrained air increases with an increase in the ratio of fine to coarse aggregate and with increased slump. As the cement content increases, a greater amount of the agent is required to produce the same air content; this may be due partly to the decrease in the amount of fine aggregate required. Since the amount of air entrained seems to depend on the quantity of fine aggregate, the optimum percentage of air should probably be based on the amount of fine aggregate. The average amount of air entrained in ordinary concrete is generally about 1 per cent., but varies from 0.8 per cent. to 2.7 per cent. A small increase greatly improves the resistance to freezing and thawing, concrete having an air content of about 3 per cent. having a markedly improved durability. For cement contents of 400 lb. to 600 lb. per cubic yard the greatest increase in durability with no appreciable reduction in strength appears to be reached when the air

content is about 4 per cent., which is considered to be about the optimum for concrete mixtures containing coarse aggregate up to  $1\frac{1}{2}$  in. Apparently, further study is necessary to determine what is the optimum amount of air in concrete for various purposes, and it may be that there is an optimum air content, based on the mortar content of the concrete, suitable for all purposes.

Appreciably less improvement is noted in the durability of concrete containing aggregates known to produce concrete of poor durability. Apparently there is a critical cement content, in excess of 650 lb. per cubic yard, beyond which little improvement in durability can be obtained by entraining air, but this is a controversial point, and more experience is needed. The increase in durability indicated by laboratory tests amounts in some cases to several hundreds per cent., and site observations confirm this. The increased air content produced by the air-entraining agent, rather than the agent itself, is probably responsible for the improved durability, since when entrained air is removed from freshly-mixed concrete the improvement is lost. The dispersed minute air bubbles probably provide expansion chambers, which may relieve the pressure created in the concrete due to volume changes caused by changes in temperature and moisture and by the expansion of ice. The lower water-cement ratio and the reduction in the number of capillaries in the mortar also probably contribute to the greater durability. The air voids appear to be mostly less than 50 microns.

Entrained air acts as a lubricant, making the concrete more plastic and workable and less subject to bleeding, and tends to reduce separation except that separation of fine aggregate is more likely to occur when the amount of sand exceeds the optimum. Entrained air increases the cohesiveness of the mixture, retards settling of the aggregate during transport, and increases the plastic deformation.

When air is entrained and the slump maintained constant through reduction in the proportions of water and cement, the workability is found to be better than that of concrete without entrained air. A given percentage of entrained air in a lean mixture produces a greater improvement in workability and plasticity than in richer mixtures, thus permitting greater reduction in the water-cement ratio of the leaner mixtures.

Air-entrainment without other changes in the mixture reduces the compressive and bending strength, but the reductions can often be avoided by changes in the mixture, mainly by a reduction in the water-cement ratio and the ratio of sand to cement. Such changes in mixtures having 376 lb. or less of cement per cubic yard often result in concrete of greater strength than the corresponding ordinary concrete. When the amount of cement is kept constant and the water-cement ratio and sand content are reduced, the effect on the strength varies from a slight increase for mixtures of low cement content to a decrease of 3 to 5 per cent. in strength for each 1 per cent. of air entrained in mixtures of greater cement content.

The resistance to abrasion of concrete containing less than 6 per cent. of air differs little from that of ordinary concrete, but there is progressive decrease in

the resistance as the air content increases, so that when the amount of entrained air approaches 10 per cent. resistance to abrasion is very low, although the concrete is extremely resistant to freezing and thawing.

The slump test shows that air-entrained concrete is apparently more sensitive to changes in water content than is ordinary concrete. Air-entrained concrete having a slump of 2 in. or more is more workable than ordinary concrete having the same slump.

The introduction of entrained air into an otherwise normal concrete results in a marked increase in the volume of the mortar. To maintain the same slump and cement content, it is necessary to reduce the quantities of water and fine aggregate.

An increase in the ratio of fine to coarse aggregate results in an increase in the air content of the mix. Available data indicate that the coarse aggregate has little effect, except as it affects the amount of sand required.

The addition of calcium chloride (say 2 per cent. by weight of the cement) increases the amount of air entrained from about 0.8 per cent. to 1.5 per cent., and the strength of air-entrained concrete at a given age is increased by about the same amount as when calcium chloride is used in ordinary Portland cement concrete. The use of calcium chloride does not affect the increase in workability resulting from the entrained air. The use of calcium chloride to promote rapid setting at low temperatures is probably more beneficial with air-entrained concrete since low temperatures retard the growth of strength of air-entraining concrete slightly more than of ordinary concrete.

When the agent is not dependent on reaction with the alkalis in the cement for its air-entraining property, the maximum amount of air is entrained after about five minutes' mixing in a small tilting-drum mixer, but the amount of air decreases as the mixing time increases.

Air-entrained concrete in the plastic state has a marked tendency to "bleed" less than comparable ordinary concrete, thereby reducing the occurrence of laitance, and results in less separation of the mortar from the underside of pieces of coarse aggregate.

The consolidation of air-entrained concrete by vibration generally results in a slight decrease in the air content, which may be due to the removal of large air bubbles incidentally entrapped in the concrete as in ordinary concrete. In prolonged vibration some of the entrained air may be removed.

The amount of air entrained decreases as the temperature of the concrete increases, especially in the range from 60 deg. to 80 deg. F. The decrease in the air content per unit increase in temperature is apparently more marked as the slump of the concrete increases. The modulus of elasticity of concrete having the same water-cement ratio and the same proportions of aggregates is reduced from 2 to 3 per cent. for each 1 per cent. of air entrained. The few data available indicate that when the amount of cement is not less than 520 lb. per cubic yard entrainment of air increases the resistance to sulphate attack, especially for cement with small proportions of  $C_3A$ . The bond with reinforcement is less with

air-entrained concrete, but this reduction may be checked, as are the reductions in compressive and bending strength, by maintaining the air content of the concrete at the optimum.

For the proper control of air-entrained concrete the amount of air in the mixture must be known. Among several methods by which the air content may be accurately determined are the rolling method, the pressure gauge, the hook gauge, and the gravimetric method, all of which give reasonably satisfactory results when used correctly.

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### The Microscopical Study of Portland Cement Clinker.

THE results of a photographic study of 21 Portland cement clinkers are given in a paper by Mr. L. S. Brown, published in the Journal of the American Concrete Institute for May 1948. The study was undertaken in connection with the production of the cement to be used in a study of the behaviour of cement and concrete over a long period, and the principal objective was to determine the actual mineral compositions of the clinkers of which the cements used in these long period tests are made. Other objectives were (1) to determine the characteristics of all the observable minerals and to formulate a method for their determination and measurement; (2) to compare the measured mineral compositions with respect to the weight of 1 litre of clinker  $\frac{1}{4}$  in. to  $\frac{3}{8}$  in. in size and the size of the clinker; and (3) to compare the mineral analyses with the calculated composition, the clinker glass as determined by the heat of solution method, and the heat of hydration at different ages. The studies showed that nine entities were regularly determinable; these were  $C_3S$ ,  $C_2S$ ,  $C_3A$ ,  $C_4AF$ , free  $CaO$ , free  $MgO$ , a dark prismatic mineral, glass, and a microscopically undifferentiated complex.

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# C E M E N T

## AND

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